

## RELAXATION IN RANDOM BINARY COMPOSITES

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**Abstract :** Relaxation behaviour in a two-component carbon-wax composite subjected to a voltage greater than onset voltage ( $V_o$ ) is presented. Relaxation from nonlinear states (between  $V_o$  and  $V_S$ ) is marked by a single stretched exponential ( $\beta \sim 0.4$ ) whereas that from higher voltages ( $>V_S$ ) is characterised by two exponentials (non-Debye type) with  $\beta \sim 0.4$  (stretched or sub-exponential) and  $\sim 1.4$  (super exponential) in the early and later time respectively.

**Keywords :** Composites, nonlinear, dynamical conductance, sub- and super exponential relaxation, onset voltage, saturation voltage.

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### 1. Introduction

If a dynamical system in equilibrium is perturbed or disturbed by external parameter like voltage ( $V$ ), temperature ( $T$ ), external magnetic field ( $H$ ) etc, it takes variable length of time depending on the dynamics of the system and the magnitude of these external parameters to relax back to the equilibrium state. The cooperative interaction between the constituent microscopic elements drives the systems towards equilibrium. The time taken by the system to come to the equilibrium state from the disturbed state is characterised by the relaxation time ( $\tau$ ). This relaxation time is found to depend on the dynamics of the system. The concept of  $\tau$  can be easily understood in an *LCR* circuit by solving the first order differential equation for the decay of charge in a fully charged capacitor.

The time evolution of the small departure  $\Delta$  from equilibrium determines the decay rates and the relaxation behaviour in these systems. The linear relation connecting  $\Delta$  is given by

$$\frac{d\Delta}{dt} = -\frac{\Delta}{\tau} \quad (1)$$

where  $\tau^{-1}$  is the rate at which the system is driven towards equilibrium from perturbed state. This relation does not take into account the detailed microscopic mechanism [1]. The relaxation time ( $\tau$ ) in a percolative systems shows a critical slowing down near percolation threshold ( $p_c$ ) and diverges at  $p_c$  [2] as:

$$\tau \sim \xi^z \sim (p - p_c)^{-\nu z} \quad (2)$$

where  $z$  is the dynamic exponent and  $\xi$  is the correlation length with an exponent  $\nu$  defined by  $\xi \sim (\Delta p)^{-\nu}$  where  $\Delta p = p - p_c$  [3, 4]. But in the glass systems,  $\tau$  shows a completely different behaviour described by the Vogel-Fulcher law [5, 6]:

$$\tau \sim \exp[1/(T - T_0)] \quad (3)$$

where  $T_0$  is a fitting parameter and the relaxation time diverges usually at a temperature  $T_0$  different from  $T_g$ , the glass transition temperature ( $T_0 < T_g$ ). The response function  $\Delta(t)$  is of the conventional Debye form for a single value of  $\tau$ . However, a distribution of  $\tau$  values and its time dependence may lead to non-Debye type relaxation of the form

$$\Delta(t) \sim \exp[-(t/\tau)^\beta]. \quad (4)$$

$\beta = 1$  corresponds to the standard Debye form of relaxation and  $\beta \neq 1$  gives the stretched or super exponential relaxation behaviour and holds for dielectric, optical, recombination, mechanical, volume, enthalpy, conductivity relaxation etc., independent of whether the relaxation species is an electron, ion, dipole, polymer segment or polymer chain. Recently, this stretched exponential relaxation has been observed in various types of systems like amorphous hydrogenated silicon [1], neural networks [2], spin glasses [7], charge density wave [8], supercooled liquids [9, 10] and percolating systems [11-13]. This non-Debye-like relaxation behaviour is generally explained in terms of two scenarios. In the disordered structure, there are a large number of channels for the response function to propagate through the system. Each channel acts as an independent relaxational (Debye-like) process with a particular relaxation time. The overall response of these independent parallel processes with a distribution of relaxation times,  $n(\tau)$  is the non-Debye like behaviour. In the

other model, these parallel independent processes are assumed to be strongly coupled so that the dynamics is severely constrained, one needing to relax before another can do so; even if each relaxation site has the same value of  $\tau$ , the coupling between them ensures that the time domain is effectively stretched, thereby ensuring a non-Debye response. Recognizing the strong similarities of relaxation processes in different random systems like glasses, spin-glasses, polymers, viscous fluids, disordered dielectrics, Ngai et al. [7] found that the common origin of such stretched exponential relaxation behaviour is due to the strong coupling of the relaxing modes to low-energy excitation showing infrared divergence. In these studies the focus was on the parameter  $\tau$  as a function of magnetic field ( $H$ ), temperature ( $T$ ) or conducting fraction ( $p$ ).

A composite system consists of conductors and insulators and is characterised by the conductor fraction ( $p$ ). For low value of  $p$ , the composite shows insulating behaviour. If the value of  $p$  is increased from low, at a certain value of  $p$  known as percolation threshold ( $p_c$ ), the composite starts conducting for the first time. At  $p_c$ , a sample spanning cluster (an incipient infinite cluster) is formed. This percolation cluster is known to be fractal [3, 4]. Near  $p_c$  various quantities like correlation length ( $\xi$ ), macroscopic resistance ( $R$ ), percolation probability ( $P(p)$ ) and noise power  $S_v(f)$  at a frequency ( $f$ ) diverge with their own critical exponents. Resistance tends to diverge as  $p_c$  is approached from above:  $R \sim (\Delta p)^{-t}$ , where  $t$  is the conductivity exponent in the limit of  $V \rightarrow 0$ . Measurements of these quantities near  $p_c$  reveal that the response is very sluggish and the system takes several hours to relax back from nonlinear state to linear state. To materialise this observation, the relaxation time  $\tau$  is experimentally measured as a function of voltage in a carbon-wax composite.

## 2. Experimental

Relaxation measurements were carried out on the disc-shaped (10 mm in diameter, 2 mm in height) carbon-wax samples under dc excitation by sending constant currents at the room temperature. The samples used for studying the relaxation behaviour are similar to the ones as in ref. [14, 15] where further details can be found. This system has a low value of  $p_c$  of 0.76% by volume and the transport exponent  $t$  equal to 2.1. Resistances of the samples chosen in the present study ranged from few tens of k $\Omega$  to M $\Omega$ . All measurements were performed using pressed circular brass electrode contacts in the two probe configuration. A programmable constant current source (Keithley, Model 224) was used to send a constant current through the sample and the sample was allowed to stabilise for almost one hour at this current. The voltage across the sample was recorded by using a digital multimeter with an integral time

of 16.66 msec and typically 500 data were stored in a personal computer at an interval of 250 msec. These data were then averaged to get the average voltage across the sample. The current was then adjusted to a low value such that sample is expected to relax back to the linear regime. As soon as the current was set at this value, the corresponding voltage recording was started and the data were stored in a file at an interval of 250 msec. The interval was then changed at some other value and the data were stored. The voltages were recorded at four such intervals for fixed value of current. The length of such intervals were chosen according to the resistance of the sample and the voltage from which the sample was allowed to relax. The intervals were larger for the larger resistances and the large voltages. Then the current was set at an another value and the same procedure was repeated.

### 3. Results and discussions

Fig. 1 shows schematically the behaviour of dynamical conductance ( $dI/dV$ ) as a function of the dc bias ( $V$ ) at a fixed  $T$  and  $p$  close to the percolation threshold. At very low bias we have the linear regime ('a') where the conductance is practically constant. Relaxation in this regime is too fast to be measured. As  $V$  is increased there is a crossover from linear to nonlinear regime at a bias  $V_0$  called the 'onset' bias or voltage and the corresponding current is called onset current  $I_0$ . This onset current  $I_0$  scales with the linear conductance  $\Sigma_0$  [14, 16] as

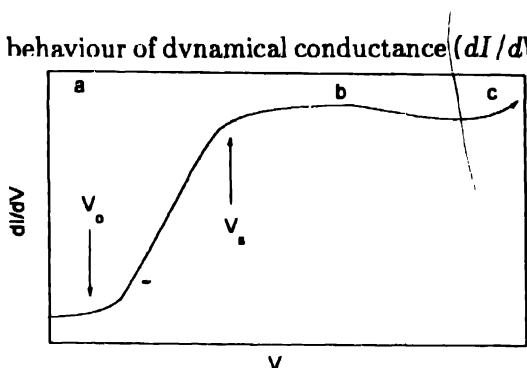


Fig. 1: A schematic diagram showing behaviour of dynamical conductance  $dI/dV$  as a function of dc bias. The regions are marked as follow: (a) onset of nonlinearity; (b) saturation; (c) joule heating and breakdown regime.

$$\Sigma_0^x \quad (5)$$

where  $x$  is the onset exponent. The value of this onset exponent in composite systems is 1.4 [14, 17]. As the bias increases to  $V_s$  the conductance still keeps on increasing but at a lesser rate. With further increase in the bias,  $dI/dV$  approaches asymptotically a constant value, corresponding to the saturated state ('b') [15]. The saturated state is fairly wide in the voltage scale. The nonlinear regime as shown in the figure may be also called 'tunneling' regime. When a sample relaxes from this region, it takes about few minutes to relax

back to the linear region (marked by 'a') and a single value of  $\beta$  is observed. On the other hand, for relaxation from the saturated state, the time to come back to the linear regime is of the order of several hours. Two values of  $\beta$  are observed ( $\sim 0.4$  and  $\sim 1.4$ ). The region marked 'c' is actually the Joule or irreversible regime where the large sample current may cause  $\Sigma$  to decrease a little before leading to irreversible state of breakdown or destruction. This regime is of no interest in the present work.

The sample is initially biased at a voltage  $V(=IR(I))$  by sending a current  $I$  through it where  $R(I)$  is the resistance of the sample at a current  $I$ . When the value of the current is set to a lower value  $I'$  the voltage across the sample should be  $V' = I'R(I)$ , if it could be measured. But the system undergoes a very rapid relaxation to a resistance  $R(t=0) > R(I)$  so that the experimentally measured voltage  $V_{meas}$  is somewhat greater than the voltage  $V'(t=0)$ . With time,  $R(I)$  increases towards its linear value  $R_0$  and hence  $V_{meas}$  also increases.  $V_{meas}$  is normalized by its maximum value and is denoted

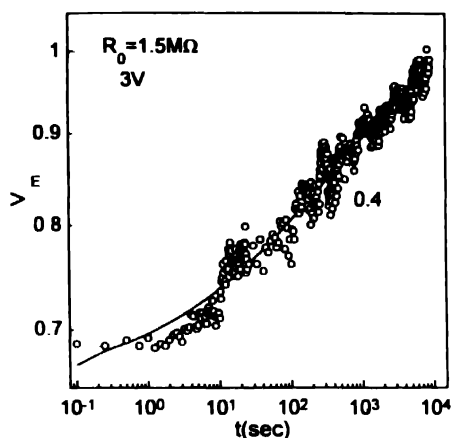


Fig. 2: Log-log plot of normalized voltage  $V_m$  vs time  $t$  for a sample of linear resistance  $R_0 = 1.5 \text{ M}\Omega$  at 3V.

The value of  $\beta$  is indicated in the figure.

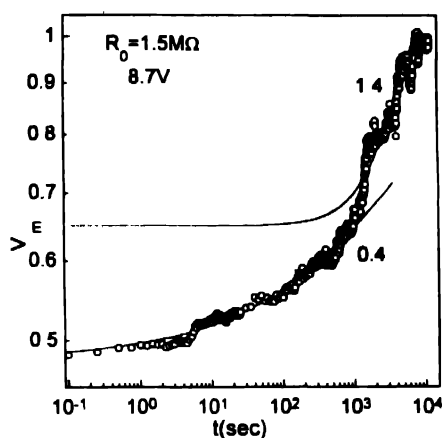


Fig. 3: Log-log plot of normalized voltage  $V_m$  vs time  $t$  for the same sample as shown in Fig. 2 at 8.7V. The two values of  $\beta$  are indicated in the figure.

by  $V_m$ . Fig. 2 shows the typical plot of  $V_m$  vs time ( $t$ ) for a sample of linear resistance  $R_0 = 1.5 \text{ M}\Omega$  at 3V. The solid line is a fit to the data by the function:

$$V_m(t) = A_0 \exp[-(t/\tau)^\beta] \quad (6)$$

where  $A_0$  is a prefactor. The value of  $\beta$  is found to be  $\approx 0.4$  as indicated in the figure. By measuring the total charge sweeping out from the band-tail states, Kakalios et al. [1] found almost the same value of  $\beta (= .45)$  in hydrogenated amorphous silicon at the room temperature. The exponent  $\beta$

was found to depend on the temperature and increase linearly with it. They explained the stretched exponential behaviour from time dependent relaxation rate. Kriza et al. [8] measured the decay of polarization current as a function of time  $t$  in a charge-density-wave compound  $K_{0.3}MoO_3$  well below the Peierls transition temperature ( $T_p = 180\text{ K}$ ) and found  $\beta=0.7$ , higher than the value observed in the present study. This result was explained by assuming the strong coupling between the different relaxation rates. Recently, Laignere et al. [13] experimentally observed the dynamical rupture in a heterogeneous composite of insulating epoxy resin and conducting carbon microbeads. At a current greater than a certain value which leads to irreversible electrical breakdown, the resistance of the composite increases with time and follows a power law behaviour with a exponent  $\approx 0.65$ . It may be noted that the samples were in the breakdown regime. So one cannot be sure whether the system reaches equilibrium state or not. A qualitative physical picture for this observation was rationalised by assuming the coupling between the Joule heating due the large current or voltage and positive temperature coefficient of the system resistance. All the works cited above including the present one deal with the relaxation in the reversible regime but this work is done in the irreversible regime. This does not allow comparison with this work

$V_m$  vs  $t$  data at  $8.7\text{ V}$  has been shown in a log-log plot in Fig. 3 for the same sample as in Fig. 2. Here the sample is allowed to relax from the saturated state i.e from a voltage higher than the saturation voltage  $V_S$ . The data could not be fitted to a single function as in eqn. (6). It was found that the data can be divided into two sets and separately fitted by the above mentioned function as in Fig. 2. We get two values of  $\beta$  as indicated in the figure. Thus the relaxation measurement in the high voltage ( $>V_S$ ) confirms that there are two rates by which the system relaxes to the state of zero-voltage resistance. The early time exponent agrees well with the reported value but the later time exponent ( $\sim 1.4$ ) is observed for the first time in a real experiment. Ghosh et al. [2] also found the value of  $\beta$  greater than unity ( $\beta \sim 1.3$ ) in a computer experiment by using

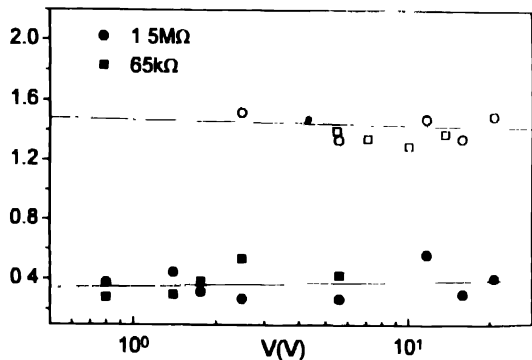


Fig. 4: Semi-log plot of  $\beta$  vs voltage  $V$  for two samples. One is the same as shown in Fig. 2 and 3 and other sample is of linear resistance  $65\text{ k}\Omega$ . The solid lines are guides to the eye.

antiferromagnetic interaction with the high value ( $\sim 15$ ) of the ratio of two exchange interaction in opposite sign.

In Fig. 4 the  $\beta$  values for two carbon-wax samples of linear resistances as shown in the figure have been plotted against the voltage  $V$ . This figure clearly indicates the existence of two  $\beta$  values and that these values are practically independent of  $V$ . The dependence of  $\tau$  on the conducting fraction  $p$  will be discussed elsewhere [18].

#### 4. Conclusion

In conclusion, we measured the voltage-dependent relaxation time in a metal-insulator composite in the nonlinear regime and found both sub- and super-exponential behaviour in relaxation.

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